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Mechanical deformation of $KD_{2x}H_{2(1-x)}PO_4$

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The deformation behavior of rapidly-grown tetragonal $KD_{2x}H_{2(1-x)}PO_4$ (KDP and DKDP) single crystals, with a deuteration degree x of 0.0, 0.3, and 0.6, is studied by nanoindentation with a 1 μm radius spherical indenter. Within experimental error, the deformation behavior is found to be independent of deuterium content and different for (001) and (100) surfaces. Multiple discontinuities (so called "pop-in" events) in force–displacement curves are observed during indentation loading, but not during unloading. Slip is identified as the major mode of plastic deformation in DKDP, and pop-in events are attributed to the initiation of slip.

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Single-crystal potassium dihydrogen phosphate, KDP (KH_2PO_4), and its deuterated form DKDP ($KD_{2x}H_{2(1-x)}PO_4$) are the most common hydrogen-bonded ferroelectrics.[1] These materials also find important applications as light frequency converters and Pockels cells in lasers, particularly in large-aperture high-power laser systems.[2] A relatively low threshold for damage formation at light intensities well below the intrinsic laser-induced breakdown threshold in KDP and DKDP optics is currently one of the most challenging scientific and technological issues for large-aperture lasers.[3–5] Laser-induced damage (LID) occurs when a high-intensity laser beam with photon energies well below the fundamental band gap exhibits strong localized absorption in the crystal.[6] The LID formation is due to ultrafast local material melting, resulting in plastic deformation and fracture of the surrounding material. Hence, studies of the physical processes controlling the deformation and fracture behavior of KDP and DKDP crystals are of significant importance to understanding evolution of LID in these materials.

The mechanical properties of single-crystal KDP have previously been studied using conventional Vickers micro-hardness testing (see, for example, Refs. 7–11). However, as has recently been discussed in detail by Fang and Lambropoulos,[10] there is still an apparent controversy regarding the microhardness of different faces of tetragonal KDP crystals, also complicated by the influence of the orientation of the edges of the pyramidal (Vickers) indenter relative to the crystallographic directions. In addition, it has been reported in Refs. 9 and 11 that the Vickers hardness of KDP can be significantly affected by impurities introduced during crystal growth. The hardness of $KD_{2x}H_{2(1-x)}PO_4$ (with quoted x values of 0.00, 0.18, 0.50, and 0.95) has previously been studied by microindentation by Shaskol'skaya et al.,[7,8] who have shown that the room-temperature Vickers hardness decreases from 1.48 to 1.28 GPa with an increase in (bulk) deuteration x from 0 to 0.95.

We are not aware of any previous studies of single-crystal KDP or DKDP by depth-sensitive nanoindentation, a more powerful technique for studying deformation behavior.[12] Hence, in this letter, we report on the main features of the deformation behavior of singe-crystal $KD_{2x}H_{2(1-x)}PO_4$ during nanoindentation. We use a spherical indenter which produces more uniform stress fields in the material as compared to the case of pointed indenters. We also use low loads ($\leq$ 10 mN) so that the sample cracking is less likely. Our results reveal differences in the mechanical properties for the two main faces of the tetragonal structure of DKDP — (001) and (100). In contrast to previous results by Shaskol'skaya et al.,[7,8] we also show that, within experimental error, the mechanical properties of DKDP are not affected by deuterium content.

The z- and x-cut [i.e., (001)- and (100)-oriented] tetragonal $KD_{2x}H_{2(1-x)}PO_4$ single crystals (with x = 0.0, 0.3, and 0.6) used in this study were grown by a rapid growth method at LLNL, as described in detail elsewhere.[2] The deuteration degree (x) was determined by elastic recoil detection analysis, as discussed elsewhere.[13] It has been shown in Ref. 13 that, due to the deuterium–hydrogen exchange, the degree of deuteration in the near-surface layers of DKDP crystals stored at ambient conditions significantly decreases within the first several days after sample polishing. Hence, in order to study the effect of deuteration on the mechanical properties, as-received KDP and DKDP samples were polished with H_2O and D_2O, respectively, and subjected to the nanoindentation testing within several minutes after water polishing. Our Rutherford backscattering/channeling spectrometry study revealed good crystal quality of the $\sim$ 1 μm-thick near-surface layers in as-polished samples.

Mechanical testing was done with a Hysitron TriboScope nanoindentation system with an $\sim$ 1 μm radius spherical diamond indenter. This indentation system, installed on a Digital Instruments Dimension 5000 scanning probe microscope (SPM), and the indenter tip were calibrated by indenting fused silica and Al single crystals. A series of both partial and continuous load–unload indents was carried out. All indents were performed at room temperature. The partial load–unload data were analyzed using the method of Oliver and Pharr[14] to extract the hardness and elastic modulus as a function of indenter penetration. After indentation, residual impressions were examined using the TriboScope *in-situ* imag-

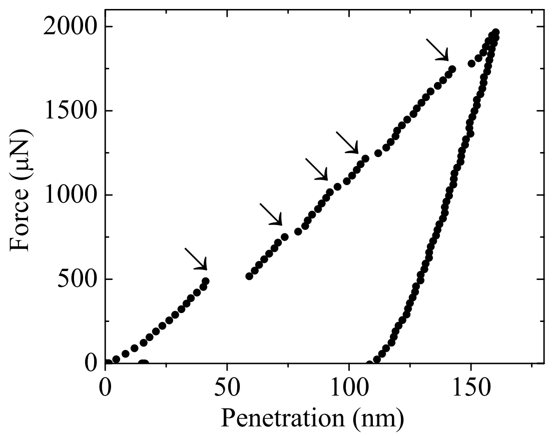

FIG. 1: Typical continuous load–unload curve of (001)-oriented single-crystal KDP. The maximum load is 2 mN. Arrows denote multiple pop-in events.

ing capability to check for evidence of cracking and and pile-up/sink-in.[15] Such *in-situ* imaging was done with the same 1 μm radius spherical diamond tip as used for indentation.

A typical continuous load–unload force–displacement curve of (001)-oriented KDP is shown in Fig. 1. This figure clearly illustrates that multiple discontinuities (or “pop-in” events) in the force–displacement curves occur during loading. No discontinuities have been observed on unloading. Results for 10 typical indents for z- and x-cut samples show that the critical load for the first pop-in, which corresponds to the *elastic–plastic threshold*, appears to be independent of deuterium content and the loading rates used (varied from 80 to 2500 μN/s) and occurs at loads of 566 ± 87 and 225 ± 52 μN for (001) and (100) surfaces, respectively. An analysis of nanoindentation data also reveals that the larger the load required for the first pop-in to occur, the larger is the length of the indenter excursion during the pop-in event. As a result, the maximum penetration of the indenter is essentially independent of the number of pop-in events during loading. Such an indenter excursion length during the first pop-in event was found to be 14 ± 4 and 5 ± 2 nm for the (001) and (100) surfaces, respectively.

An analysis of partial load–unload data for (001)- and (100)-oriented $KD_{2x}H_{2(1-x)}PO_4$ reveals that the average contact pressure [or (Meyer) hardness] H and Young’s modulus E remain essentially constant over the indenter penetration depth. The values of H and E for (001) and (100) surfaces of DKDP, as given in Table I, are found to be independent of D content, within experimental error. Previous microindentation studies of KDP have reported a rather wide range of H ($\sim 0.8 - 1.9$ GPa) values, depending on crystal growth conditions, indentation load,

TABLE I: Values of hardness (H), Young’s modulus (E), and the critical load for the elastic–plastic transition (P_{th}) for (001)- and (100)-oriented $KD_{2x}H_{2(1-x)}PO_4$ single crystals, as measured with a 1 μm spherical indenter.

	H (GPa)	E (GPa)	P_{th} (μN)
(001)	2.0 ± 0.2	44 ± 3	566 ± 87
(100)	1.6 ± 0.2	46 ± 3	225 ± 52

and the orientation of the Vickers indenter relative to the crystallographic directions.[7–10] Hence, the values of H determined in the present spherical nanoindentation study are within the range of the values previously measured by Vickers microindentation testing. It should also be noted that, although Table I shows essentially the same Young’s modulus (within experimental error) for (001) and (100) surfaces, a slight orientation dependence of E is not unexpected according to calculations from Ref. 10.

The apparent controversy between our results and data reported by Shaskol’skaya et al.[7,8] on the effect of deuteration on the hardness of $KD_{2x}H_{2(1-x)}PO_4$ can be explained as follows. As mentioned above, we have recently found that the degree of deuteration in the near-surface layers of DKDP crystals stored at ambient conditions significantly decreases within the first several days after sample polishing. Hence, the apparent difference in H for crystals with different bulk values of x could be attributed to the effect of tensile lattice stress associated with the D/H exchange process, as discussed in detail in Ref. 13. In addition, as also pointed out by Shaskol’skaya et al.,[7,8] the difference in hardness for DKDP crystals with different deuteration studied in Refs. 7 and 8 can be related to variations in types and concentrations of lattice defects and impurities. Indeed, different crystal growth conditions are typically used for the growth of crystals with different deuteration.[2]

It is well known that accurate determination of H and E from nanoindentation data requires a low level of pile-up and sink-in.[15,16] Figure 2 shows typical cross-sections of residual impressions produced in (001)-oriented KDP by indentations to different maximum loads, as measured by SPM.[17] This figure reveals negligible pile-up and sink-in during relatively low load indentation used to identify the values of H and E (note the difference in the scale for vertical and horizontal axes in Fig. 2). The negligible effect of pile-up/sink-in on the H and E values is also supported by the fact that E remains essentially constant over the indenter penetration depth, as discussed above. However, SPM shows that pile-up around the impression increases for larger maximum loads. The presence of such pile-up for large loads is expected given that KDP and DKDP are relatively soft materials (see Table I). No cracking has been observed by SPM for the loads used in this study (≤ 10 mN).

Previous selective-etching studies[7,8] of indentation-

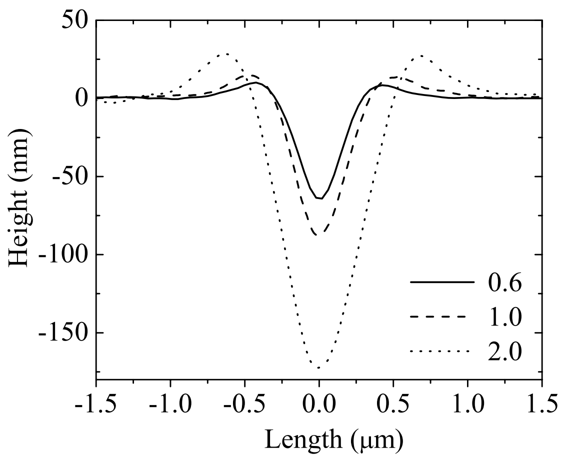

FIG. 2: Typical cross-sections of residual impressions produced in (001)-oriented KDP by continuous load–unload indentation with a 1 μm spherical indenter to maximum loads indicated in the legend (in mN).

produced dislocations in KDP and DKDP crystals have clearly demonstrated that slip is the major mode of plastic deformation in these materials. The following active slip systems in KDP and DKDP have been identified:[8] {110}, {101}, {112}, {123}, and {010}. The difference in the mechanical properties of (001) and (100) surfaces, observed in the present study, can be attributed to the fact that different slip planes are activated during the indentation of different facets of the crystal. Indeed, selective-etching studies of Shaskol'skaya et al.[8] suggest that more slip systems are involved in the deformation process during the indentation of the (100) surface, as compared to the case of the (001) surface.

We suggest that slip is also responsible for the pop-in events observed during loading. Indeed, pop-in events (overloading effects) are indicative of important physical processes occurring during deformation, such as the initiation of slip and/or pressure-induced phase transformations (see, for example, Ref. 18). Previous nanoindentation studies have shown that such an overloading behavior (a single or multiple pop-in events) is typical for a number of single-crystal insulators and semiconductors (such as sapphire, GaAs, InP, GaN, and ZnO), where plastic deformation involves slip via the punching out of dislocations (see, for example, Refs. 18–21). Previous transmission electron microscopy and Raman spectroscopy studies have revealed no evidence for pressure-induced phase transformations during spherical indentation at room temperature in all the insulators and compound semiconductors studied.[18–21] In such cases, slip has been identified as the *only* physical mechanism responsible for plastic deformation under indentation conditions similar to those used in the present study. Hence, a comparison of indentation results for KDP with data known for other insulators and compound semiconductors strongly supports an argument that slip is the sole mechanism for plastic deformation of $KD_{2x}H_{2(1-x)}PO_4$ during room-temperature spherical indentation. In addition, although densification by phase transformations (to an orthorhombic structure) has previously been observed in KDP in diamond anvil cell experiments,[22] the hydrostatic pressure needed to induce this phase transformation is ~ 7.5 GPa. This is well above the maximum pressure realized in this study ($<$ 2 GPa) before plastic deformation occurs.

Finally, it should be noted that relatively low values of the elastic–plastic threshold and H of $KD_{2x}H_{2(1-x)}PO_4$ are, in fact, not unexpected, given the relatively low melting points ($T^{melt}_{\mathrm{KDP}} \approx 260$ °C and $T^{melt}_{\mathrm{DKDP}} = 250$ °C)[23] and large ionicity of these materials. Indeed, the activation energy for dislocation propagation during slip may be expected to scale with the melting point.[24] Furthermore, the ionic nature of chemical bonding between K and PO_4 groups is expected to facilitate the nucleation and propagation of dislocations via the ease of bond-angle distortion as compared to the case of purely covalent bonding.[24]

In conclusion, the deformation behavior of single-crystal bulk $KD_{2x}H_{2(1-x)}PO_4$ has been studied by nanoindentation in combination with *in-situ* SPM imaging. Multiple discontinuities have routinely been observed during loading when the maximum load is above the elastic–plastic threshold. The mechanical properties have been found to be independent of deuterium content and different for (001) and (100) surfaces. Slip, initiation of which appears to cause pop-in events, is concluded to be the major mode of plastic deformation in KDP and DKDP. The relatively low values of the elastic–plastic threshold and hardness, revealed in this study, need to be taken into account in handling and processing KDP and DKDP optics and may also contribute to the relatively low values of the laser-induced damage threshold typically observed for these materials.

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